method have been described elsewhere[33,34] and need not be repeated here. The θ and ϕ geometrical parameters were taken from the reported structure of octachlorobis(adeninium)tricopper(II) tetrahydrate.[4] For each of the site calculations a nitrogen atom was placed on the assumed z axis. The α_4 crystal field parameters were assumed[33,34] to be α_4(nitrogen) = 10 000 cm^{-1}, α_4(terminal chloride) = 5000 cm^{-1}, and α_4(bridging chloride) = 4500 cm^{-1}. The calculated "d–d" transition energies for the central copper ion in the trimer are 7930, 14 210, 14 350 and 15 830 cm^{-1} and for the terminal copper ions 6740, 10 570, 11 140, and 12 800 cm^{-1}. These calculated transition energies are in reasonable accord with the observed spectrum (Figure 4). The calculations indicate that transitions below 500 nm are not due to "d–d" excitations. More importantly, the calculations show that the two types of coordination sites in the trimer give rise to ground states having predominantly d_{z^2} character, a result in full accord with the observed EPR spectrum of the trimer.

As may be seen in Figure 1, the trimers are linked by long copper–chloride bonds (3.274 Å) into chains, but it is clear from the magnetic susceptibility data that chain behavior does not obtain. A low-temperature study of the EPR of this material would be very interesting, since it is likely that these intertrimer contacts will provide orbital pathways for excited-state migration.

Acknowledgment. D. B. Brown wishes to thank the Office of the Naval Research for partial support of this research. The research was also supported by the National Science Foundation through Grant MPS74-11495 and by the Materials Research Center of the University of North Carolina through Grant DMR72-03024 from the National Science Foundation.

Registry No. $(C_5N_5H_6)_2Cu_3Cl_8$, 40906-58-9.

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Synthesis and Studies of Trimethylamine Adducts with Tin(II) Halides

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Received May 3, 1977 AIC70172U

The complexes $SnX_2\cdot N(CH_3)_3$ and $SnX_2\cdot (N(CH_3)_3)_2$, X = F, Cl, Br, and I, have been synthesized and characterized. The thermal dissociation of the adducts was studied using thermal gravimetric and differential thermal analysis as well as trimethylamine pressure measurements at temperatures from 40 to 120 °C. The free energy changes associated with the dissociation were small; the order of adduct stabilities was iodide > bromide > chloride > fluoride for both 1:1 and 1:2 adducts. Linear relationships were found between the ΔG for adducts and the complexation Mössbauer isomer shift and also with the complexation NMR chemical shift for the 1:1 adducts.

Introduction

A number of amine adducts of the various tin(II) halides have been reported,[1] but few systematic studies of such adducts have appeared. Ammonia adducts of SnX_2 molecules with acceptor:donor ratios up to 1:9 have been reported but ratios of 1:1 and 1:2 are usual. Little is known concerning the factors which influence the stabilities of such adducts. It is of particular interest to determine how the stability of adducts with a given reference base varies with the halogen in the tin(II) halide.

We wish to report here the results of our investigation of the reaction of trimethylamine with the four tin(II) halides. Both 1:1 and 1:2 adducts were prepared and their relative stabilities toward dissociation were studied by thermal analytical techniques and equilibrium dissociation pressure measurements. NMR, IR, and Mössbauer spectral parameters are also reported.

Experimental Section

Equipment. A standard glass vacuum system was employed in these studies.[2] A Labconco glovebox fitted with a recirculating system for maintaining a dry N_2 atmosphere was used for transfers under anhydrous conditions. Infrared spectra were obtained on a Perkin-Elmer Model 700 spectrophotometer either in KBr disks or in a gas cell with 8.3-cm path length and sodium chloride windows. A Beckman Model 4250 infrared spectrophotometer was employed for the range from 700 to 250 cm^{-1}. X-ray powder diffraction patterns were taken using a Debye–Scherrer camera in conjunction with a Norelco water-cooled generator fitted with a copper tube and nickel filter, operating at 35 kV and 20 mA filament current. Melting points

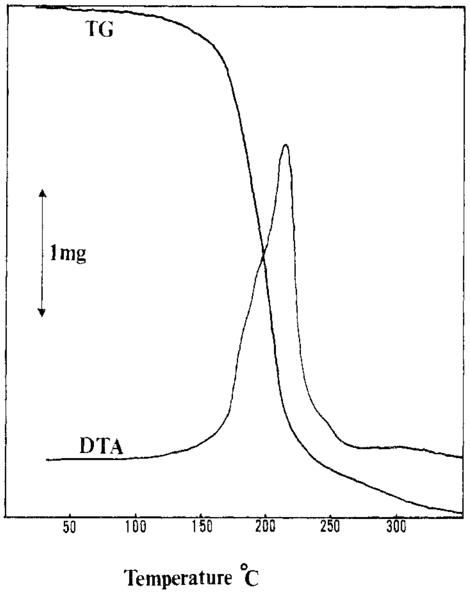

Figure 1. Typical thermal gravimetry and differential thermal analysis curves for tin(II) halide–trimethylamine adducts.

were obtained in glass capillaries (sealed with wax) on a heated block apparatus. Thermogravimetric data were obtained using a DuPont thermoanalyzer at a heating rate of 10°/min. Typical thermoanalytical curves for tin(II) halide–trimethylamine adducts are shown in Figure 1. A Varian Model T-60 instrument was employed to obtain ^{1}H NMR spectra at 60 MHz. Thermal dissociation pressures were measured in a thermostated oven under conditions chosen to provide equilibrium pressure values. Under an N_2 atmosphere, measured quantities of adduct were placed in a tube attached via an O-ring connector to a glass expansion bulb of about 1400 mL capacity fitted with a mercury manometer. All parts of the apparatus were situated within the oven. The sample tube was cooled with dry ice, the vessel evacuated, and the system isolated from the vacuum line by closing a Teflon valve. The sample was allowed to warm to room temperature where the first pressure measurement was made using an external cathetometer for viewing the mercury manometer through a window in the oven. Samples were slowly warmed to the temperatures where pressure measurements were to be taken with a fan operating inside the oven to prevent thermal gradient effects. Measurements were made at 20° intervals in the range from 40 to 120 °C in which range reasonably good reversibility was observed; above 130 °C the dissociation became irreversible. The evolved gas was shown to be trimethylamine by comparison of its IR spectrum with that of an authentic sample. Equilibrium dissociation pressure measurements for all but the SnF_2 adducts are listed in Table II.

Mössbauer spectra were obtained on an Austin Science Associates constant acceleration spectrometer using a Northern Scientific 1024 channel analyzer for data collection. Approximately 5×10^5 points were collected in baseline channels, and the spectrum was fitted to Lorentzian line shapes with a standard computer program.[3] A New England Nuclear ^{119m}Sn in barium stannate source was employed for all spectra. Sample thickness was chosen to contain approximately 8.8×10^{17} Sn atoms per cm^2 of sample area. The spectrometer was calibrated using Fe foil and SnO (black).

Materials. Reagent grade starting materials and solvents were employed unless otherwise noted. Trimethylamine was purchased from the Matheson Co. and used as obtained. Because of several instances where tin(IV) impurities were found to be present in significant quantities in commercial tin(II) compounds, the tin(II) halides used in this study were prepared fresh, analyzed, and stored under anhydrous conditions until used.

Tin(II) Oxide. Tin(II) oxide was prepared[4] for use as an intermediate material in the preparation of tin(II) bromide and tin(II) fluoride. In a typical preparation, 30 g of metallic tin was dissolved in 120 mL of 6 N hydrochloric acid, and concentrated ammonium hydroxide was added until the mixture reached pH 9. The white precipitate was washed three times with 2 N ammonium hydroxide solution; then the hydrous tin(II) oxide solid was heated with 120 mL of 2 N ammonium hydroxide solution at 60–70 °C overnight. After that time it was washed several times with water, filtered, and dried in vacuo.

Tin(II) Fluoride.[5] A measured quantity of tin(II) oxide was added to a slight excess of a 52% hydrofluoric acid solution in a plastic beaker and, under the protection of nitrogen, the solution was heated to 60 °C. Agitation was necessary to cause complete dissolution of SnO. The solution was cooled, whereupon white crystals formed and the entire reaction mixture was dried over potassium hydroxide, then transferred to the vacuum line and subjected to dynamic vacuum for at least 18 h to obtain anhydrous tin(II) fluoride. Anal. Calcd for SnF_2: Sn, 75.8; F, 24.3. Found: Sn, 72.5; F, 24.6.

Tin(II) Chloride. Anhydrous tin(II) chloride was obtained by dehydrating reagent grade stannous chloride dihydrate, $SnCl_2{\cdot}2H_2O$, on the vacuum line to a white powder. Anal. Calcd for $SnCl_2$: Sn, 62.6; Cl, 37.4. Found: Sn, 62.3; Cl, 37.2.

Tin(II) Bromide. A measured quantity of tin(II) oxide was dissolved in a 34% hydrobromic acid solution under a nitrogen gas stream. The quantity of the acid taken was in slight excess of a 2:1 mole ratio with the oxide. When dissolution was complete all volatile components were removed by vapor transfer on the vacuum line and the remaining solid consisted of anhydrous tin(II) bromide. Anal. Calcd for $SnBr_2$: Sn, 42.6; Br, 57.4. Found: Sn, 41.7; Br, 56.6.

Tin(II) Iodide. In a typical preparation, 6.0 g of tin metal was dissolved in 30 mL of 12 N hydrochloric acid giving a solution of tin(II) chloride dihydrate. In another vessel 13.0 g of iodine was reacted with an excess of zinc strips along with 10 mL of water and the reaction mixture was shaken until it became colorless, then filtered, and chilled in ice. The ice cold solution of zinc iodide was then added to the cold solution of stannous chloride, precipitating yellow-orange needle crystals of tin(II) iodide dihydrate. The solid was filtered off and recrystallized from dilute HCl solution. Anhydrous SnI_2 was obtained by subjecting the crystals to a dynamic high vacuum overnight. Anal. Calcd for SnI_2: Sn, 31.9; I, 68.1. Found: Sn, 32.3; I, 69.2.

Synthesis of Adducts. Tin(II) Fluoride–Trimethylamine. A measured quantity (20 mmol) of SnF_2 was placed in a 50-mL bulb attached to the vacuum line by means of an O-ring joint and a Teflon valve. The vessel was evacuated and an equimolar quantity of $N(CH_3)_3$ condensed in without solvent. The Teflon valve was closed and the system allowed to stand for 1 week at room temperature. Enough ethyl ether was condensed in to form a suspension of the white solid upon vigorous stirring and this was filtered under a stream of anhydrous nitrogen. The product, $SnF_2{\cdot}N(CH_3)_3$, was found to be very hygroscopic and subject to apparent loss of trimethylamine after a few days. Anal. Calcd for $SnF_2C_3H_9N$: Sn, 55.0; F, 17.6; N, 6.49. Found: Sn, 54.8; F, 17.4; N, 6.07. The compound showed evidence of decomposition near 70 °C but eventually melted in the range 263–267 °C. Its infrared spectrum contained the following bands (cm^{-1}): 3165 (w), 2980 (m), 2725 (vs), 2495 (vw), 1630 (w, b), 1480 (s), 1433 (vw), 1405 (vw), 1262 (w), 990 (s), 750 (m, b), and 545 (m, b). The *d* spacings in the x-ray powder diffraction pattern were as follows [*d*, Å (intensity)]: 6.50 (w), 6.14 (m), 5.86 (w), 4.34 (w), 4.12 (m), 3.70 (w), 3.54 (m), 3.50 (vvs), 3.41 (vs), 3.28 (s), 3.16 (s), 3.05 (m), 2.93 (m), 2.64 (w), 2.52 (w), 2.42 (w), 2.32 (w), 2.27 (vw), 2.11 (w), 2.08 (vw), 2.04 (s), 1.96 (m), 1.94 (s), 1.91 (m), 1.83 (m), 1.78 (m), 1.75 (s), 1.73 (w), 1.65 (w), 1.60 (m), 1.54 (w), 1.51 (w), 1.49 (vw), 1.45 (vw), 1.41 (vw).

Tin(II) Chloride–Trimethylamine. A 5.0-g (26.4 mmol) quantity of $SnCl_2$ was placed in a 50-mL flask equipped with an O-ring joint and Teflon valve adapter. About 50 mL of reagent grade dioxane, previously dried over BaO and treated with CuCl to remove peroxides, was condensed into the reaction vessel along with 26.4 mmol of trimethylamine. The Teflon valve was closed and the reaction mixture allowed to warm to room temperature with stirring. Over a period of 4 days the suspended white solid became pale yellow. After that time period the volatiles were fractionated through traps held at −78 and −196 °C revealing that essentially all the trimethylamine had been consumed. Dioxane was removed by vapor transfer with a dynamic vacuum over a period of several hours. Anal. Calcd for $SnCl_2C_3H_9N$: Sn, 47.7; Cl, 28.6; N, 5.62. Found: Sn, 48.0; Cl, 28.8; N, 5.45. The product melted with decomposition at 238–239 °C. Its IR spectrum contained the following bands (cm^{-1}): 3160 (vs), 2980 (vw), 2750 (w), 2380 (vw), 1630 (w, b), 1470 (vs), 1415 (m), 1385 (m), 1250 (w), 980 (vs), 810 (w), 680 (w), and 562 (m, b). The x-ray powder diffraction pattern of $SnCl_2{\cdot}N(CH_3)_3$ consisted of the following lines [*d*, Å (intensity)]: 6.4 (vs), 5.53 (s), 4.75 (s), 4.32 (vs), 4.10 (w), 3.87 (m), 3.39 (m), 3.07 (s), 2.93 (w), 2.75 (s), 2.64 (m), 2.58

Table I. Dissociation Measurements of Tin(II) Halide-Trimethylamine Adducts from Thermogravimetry Curves

Adduct	Sample wt, mg	Weight loss at 110 °C mg	Mole % dissociation
$SnCl_2 \cdot N(CH_3)_3$	6.04	0.19	13
$SnBr_2 \cdot N(CH_3)_3$	5.61	0.10	10
$SnI_2 \cdot N(CH_3)_3$	5.42	0.10	13
$SnCl_2 \cdot 2N(CH_3)_3$	5.27	0.67	67
$SnBr_2 \cdot 2N(CH_3)_3$	5.72	0.13	15
$SnI_2 \cdot 2N(CH_3)_3$	5.72	0.09	13

Table II. Equilibrium Dissociation Pressures (mmHg) of Adducts

Temp, °C	$SnCl_2 \cdot N(CH_3)_3$	$SnBr_2 \cdot N(CH_3)_3$	$SnI_2 \cdot N(CH_3)_3$	$SnCl_2 \cdot 2N(CH_3)_3$	$SnBr_2 \cdot 2N(CH_3)_3$	$SnI_2 \cdot 2N(CH_3)_3$
40	2.5	1.4	0.7	2.3	1.5	1.1
60	11.8	2.2	1.0	14.9	5.1	2.2
80	18.1	4.3	1.8	35.1	18.5	4.5
100	22.4	9.4	2.5	55.4	46.8	11.6
120	27.3	18.4	5.5	77.3	60.2	31.5

(vw), 2.46 (vw), 2.34 (vw), 2.17 (m), 2.11 (w), 2.05 (m), 1.94 (w), 1.86 (w), 1.75 (vw), 1.71 (w), 1.61 (w), 1.56 (w). A dissociation measurement at 110 °C derived from the TG curve for $SnCl_2 \cdot N(CH_3)_3$ is given in Table I.

The dissociation pressure of $N(CH_3)_3$ over $SnCl_2 \cdot N(CH_3)_3$ solid was measured using the device described earlier. Temperatures were carefully controlled to ensure that equilibrium dissociation pressures were obtained (Table II). It was noted that the measured pressures could be reproduced in samples not heated above about 120 °C but above that temperature irreversible processes seemed to occur. The Mössbauer spectrum of $SnCl_2 \cdot N(CH_3)_3$ at 25 °C consisted of a single peak with an isomer shift of $+2.53 \pm 0.02$ mm s^{-1} and a width at half maximum of 0.97 ± 0.05 mm s^{-1}. The ^1H NMR spectrum of the adduct in aniline solution consisted of a singlet at δ 1.83.

Tin(II) Bromide–Trimethylamine. Using the procedure described above, a measured quantity of $SnBr_2$ was combined with an equimolar quantity of $N(CH_3)_3$ yielding $SnBr_2 \cdot N(CH_3)_3$ as a hygroscopic, yellow solid, mp 212–213 °C dec. Anal. Calcd for $SnBr_2C_3H_9N$: Sn, 35.2; Br, 47.3; N, 4.15. Found: Sn, 33.1; Br, 45.3; N, 4.29. The product exhibited the following IR bands (cm^{-1}): 3100 (s, b), 2970 (m), 2720 (s), 2480 (vw), 1620 (w, b), 1465 (vs), 1405 (vw), 1370 (vw), 1250 (w), 975 (s), 810 (w), and 560 (m, b). The x-ray powder diffraction pattern contained *d* spacings as listed below: 10.76 (vs), 7.24 (vs), 6.31 (vs), 5.63 (s), 5.33 (m), 4.76 (vw), 4.52 (m), 4.12 (vw), 3.89 (w), 3.76 (w), 3.61 (m), 3.39 (m), 3.27 (w), 3.13 (s), 3.04 (w), 2.91 (m), 2.80 (m), 2.71 (m), 2.68 (m), 2.59 (vw), 2.53 (vw), 2.41 (m), 2.31 (w), 2.21 (vw), 2.15 (w), 2.12 (w), 2.02 (vw), 1.98 (w), 1.90 (w), 1.85 (w), 1.80 (vw), 1.76 (w). A dissociation measurement derived from the TG curve for $SnBr_2 \cdot N(CH_3)_3$ is given in Table I. The Mössbauer spectrum of the adduct at 25 °C consisted of a single peak with an isomer shift of $+2.55 \pm 0.02$ mm s^{-1} with a width at half maximum of 0.91 ± 0.05 mm s^{-1}. The ^1H NMR spectrum of the adduct in aniline consisted of a singlet δ 1.75.

Tin(II) Iodide–Trimethylamine. The mono adduct of trimethylamine with tin(II) iodide was prepared as described above, yielding a yellow, air-sensitive solid, mp 172–174 °C dec. Anal. Calcd for $SnI_2C_3H_9N$: Sn, 27.5; I, 58.8; N, 3.24. Found: Sn, 26.9; I, 59.8; N, 3.03. The product was more sensitive to direct air oxidation than the other 1:1 adducts, rapidly changing to brown-black upon exposure and so it was stored in vacuo. The IR spectrum of $SnI_2 \cdot N(CH_3)_3$ contained the following bands (cm^{-1}): 3125 (w), 2990 (vs), 2765 (vs), 2490 (vw), 1610 (w, b), 1475 (s), 1430 (vw), 1410 (vw), 1266 (w, b), 990 (s), 810 (w), and 533 (m, b). The x-ray powder diffraction pattern of the adduct gave the following *d* spacings [*d*, Å (intensity)]: 8.57 (w), 7.82 (vs), 5.24 (w), 4.66 (w), 4.41 (w), 4.16 (m), 3.91 (s), 3.52 (vs), 3.46 (m), 3.27 (w), 3.09 (m), 2.99 (vs), 2.80 (vs), 2.67 (w), 2.61 (vw), 2.44 (w), 3.25 (m), 2.30 (s), 2.20 (vs), 2.13 (m), 2.02 (vw), 2.01 (m), 1.98 (m), 1.88 (vw), 1.83 (w), 1.78 (w), 1.74 (w), 1.70 (w), 1.67 (vw), 1.64 (vw), 1.61 (vw), 1.59 (m), 1.50 (m), 1.48 (m). A dissociation measurement based on the thermoanalytical curve for the adduct is given in Table I. The Mössbauer spectrum of the adduct at 25 °C consisted of a single peak with an isomer shift of $+2.57 \pm 0.02$ mm s^{-1} and a width at half-maximum of 0.90 ± 0.06 mm s^{-1}. The ^1H NMR spectrum of the adduct in aniline solution consisted of a singlet at δ 1.70.

Tin(II) Fluoride–Bis(trimethylamine). A number of attempts to prepare the 2:1 adduct of $N(CH_3)_3$ with SnF_2 by direct combination in the manner described for the synthesis of the 1:1 adduct gave inconsistent results with most products containing less than the expected proportion of amine. The most effective synthesis consisted of two steps with SnF_2 first being reacted with an equimolar quantity of $(CH_3)_3N$ using ethyl ether as the solvent. The product of this reaction, after stirring 3 days at 25 °C, was a white fluffy solid which was evidently a mixture of SnF_2 and $SnF_2 \cdot N(CH_3)_3$ since it gave an analysis of about 61% tin with some consistency. This solid was filtered from the reaction mixture under nitrogen and transferred as quantitatively as possible to another reaction vessel. In the absence of solvent a 2.5:1 molar excess of $N(CH_3)_3$ was condensed into the vessel which was closed and allowed to stand at room temperature for 7 days. At the end of that period the excess trimethylamine was expanded into the vacuum line (without subjecting the product solid to prolonged dynamic vacuum) and measured. The total $N(CH_3)_3$ consumed indicated the formula $SnF_2 \cdot 2N(CH_3)_3$. The white solid product was markedly hygroscopic and readily lost $N(CH_3)_3$ at room temperature, mp 176–177 °C dec. Anal. Calcd for $SnF_2C_6H_{18}N_2$: Sn, 43.2; F, 13.8; N, 10.2. Found: Sn, 43.8; F, 13.8; N, 9.55. The IR spectrum of the product contained the following bands (cm^{-1}): 2980 (s), 2730 (vs), 2500 (w), 1635 (w, b), 1480 (s), 1434 (vw), 1410 (vw), 1264 (m), 993 (s), 755 (m, b), and 550 (m, b). This adduct as well as all the other 1:2 adducts was found to be amorphous by x-ray powder diffraction.

Tin(II) Chloride-Bis(trimethylamine). The $SnCl_2 \cdot 2N(CH_3)_3$ adduct was prepared most successfully from $SnCl_2 \cdot N(CH_3)_3$. A 6.2-g (25 mmol) quantity of the mono(trimethylamine) adduct was placed in a dry flask and 50 mL of dry dioxane condensed in along with a 1.5:1 molar excess of $N(CH_3)_3$. The vessel was closed and the contents were allowed to warm to room temperature and stir for 48 h. The product (3.5 g, 45%) was isolated as a light yellow hygroscopic solid which was filtered from the reaction mixture under an atmosphere of nitrogen and washed twice with anhydrous ethyl ether to facilitate drying. It melted with decomposition at 175–177 °C dec. Anal. Calcd for $SnCl_2C_6H_{18}N_2$: Sn, 38.9; Cl, 23.1; N, 9.10. Found: Sn, 37.4; Cl, 23.9; N, 8.13. The IR spectrum of the solid contained the following bands (cm^{-1}): 2960 (vs), 2710 (vs), 2485 (m), 1625 (m, b), 1475 (vs), 1428 (vw), 1405 (vw), 1260 (m), 984 (vs), 810 (vw), 680 (m, b), and 543 (m, b). A dissociation measurement based on the thermoanalytical curve for the adduct is given in Table I. The Mössbauer spectrum of the adduct consisted of a single peak with an isomer shift of $+2.58 \pm 0.02$ mm s^{-1} and a width at half-maximum of 0.94 ± 0.03 mm s^{-1}.

Tin(II) Bromide–Bis(trimethylamine). The adduct $SnBr_2 \cdot 2N(CH_3)_3$ was prepared by direct combination of the components with dioxane as the solvent. In a typical synthesis 7.0 g (25.1 mmol) of $SnBr_2$ was placed in 150-mL bulb and attached to the vacuum line via a detachable O-ring joint and Teflon valve adapter. A quantity of trimethylamine corresponding to a 2:1 mole ratio was condensed into the vessel along with 50 mL of dry, peroxide-free dioxane. The Teflon valve was closed and the reaction mixture allowed to warm to room temperature and stir 4 days after which volatiles were fractionated. No appreciable amount of $N(CH_3)_3$ remained and the solid product was taken directly from the reaction vessel. The product (mp 215–217 °C dec) was slightly hygroscopic but not obviously air sensitive. Anal. Calcd for $SnBr_2C_6H_{18}N_2$: Sn, 29.9; Br, 40.3; N, 7.07. Found: Sn, 28.6; Br, 38.4; N, 6.54. The product exhibited the following IR bands (cm^{-1}): 2980 (s), 2725 (vs), 2500 (m), 1600 (w, b), 1480 (vs), 1432 (vw), 1407 (vw), 1265 (m), 992 (vs), 820 (vw), and 561 (m, b). An estimate of the adduct's dissociation at 110 °C based on the TG curve is given in Table I. The Mössbauer spectrum of the adduct consisted of a single peak with an isomer shift of $+2.52 \pm 0.02$ mm s^{-1}. The width at half-maximum was 0.99 ± 0.04 mm s^{-1}.

Tin(II) Iodide–Bis(trimethylamine). Using the procedure described above, a measured quantity of SnI_2 was combined with twice the molar quantity of $N(CH_3)_3$ with dioxane as the solvent. No excess trimethylamine remained in the volatiles after the reaction, and the product was isolated as a light yellow, air-stable solid, mp 233–237 °C dec. Anal. Calcd for $SnI_2C_6H_{18}N_2$: Sn, 24.2; I, 51.7; N, 5.71. Found: Sn, 23.2; I, 52.5; N, 5.51. The IR spectrum of the product contained the following bands (cm^{-1}): 2970 (vs), 2760 (vs), 2485 (w),

Table III. Thermodynamic Functions of the Dissociation of Tin(II) Halide-Trimethylamine Adducts

Adduct	ΔH, kcal/mol	ΔS, cal/mol (80 °C)	ΔG, kcal/mol (80 °C)[a]	ΔG, kcal/mol (80 °C)[b]
$SnCl_2 \cdot N(CH_3)_3$	3.58 (0.39)[c]	15.7 (1.1)[c]	−1.98	−2.03 (0.20)[d]
$SnBr_2 \cdot N(CH_3)_3$	8.01 (0.69)	25.9 (1.0)	−1.14	−1.02 (0.10)
$SnI_2 \cdot N(CH_3)_3$	6.10 (0.35)	18.5 (1.0)	−0.44	−0.41 (0.04)
$SnCl_2 \cdot 2N(CH_3)_3$	7.08 (0.44)	26.8 (1.2)	−2.39	−2.50 (0.25)
$SnBr_2 \cdot 2N(CH_3)_3$	13.48 (0.37)	43.8 (1.1)	−1.98	−2.05 (0.21)
$SnI_2 \cdot 2N(CH_3)_3$	8.98 (0.81)	28.7 (2.4)	−1.15	−1.06 (0.11)

[a] Calculated for ΔH and ΔS (80 °C) values obtained from linear regression slope and intercept of Van't Hoff plots. [b] Obtained from $\Delta G = -RT \ln K_p$ at 80 °C. [c] Errors determined from linear regression fit. [d] Errors determined by assuming a 10% relative error limit in the pressure measurement.

1630 (m, b), 1475 (s), 1420 (vw), 1400 (vw), 1260 (w), 985 (vs), 810 (vw), 594 (m, b), and 568 (m, b). An estimate of the adduct dissociation at 110 °C, taken from its TG curve, is given in Table I. The ^{119}Sn Mössbauer spectrum of the adduct at 25 °C consisted of a single peak with an isomer shift of +2.51 ± 0.02 mm s^{-1}. The width at half-maximum was 0.97 ± 0.03 mm s^{-1}.

Results and Discussion

Divalent compounds of tin, while formally resembling carbene species, are quite different chemically, due, in part, to factors such as promotion energies and covalent bond strengths favoring the stability of the divalent state for the heavy group 4A atoms. The presence of both a lone pair and an empty orbital in the valence shell of SnX_2 compounds suggests that such species have the potential to function both as acceptors and donors. Only a few instances of the latter have been reported,[6,7] but numerous adducts between tin(II) halides and donor molecules are known.[1] The apparent preference of the tin(II) halides toward Lewis acid behavior may result from the inductive effect of the halogens enhancing the acceptor capability of the tin and restricting its donor capacity. It is noteworthy that the best characterized example of tin(II) compounds acting as donors involves $Sn(C_5H_5)_2$[7] which essentially lacks the aforementioned inductive effect.

The purpose of this work was to synthesize and characterize all the 1:1 and 1:2 adducts of the tin(II) halides with the reference base trimethylamine and to determine the relative stabilities of the adducts. The investigation was initiated in part to compare the acceptor behavior of the tin(II) halides with that of the boron(III) halides. Another objective was to evaluate NMR and Mössbauer data as criteria of adduct stabilities.

For some time it has been known[8] that BF_3 is the weakest acceptor among the latter compounds and that the order of acceptor strength toward nitrogen bases is $BF_3 < BCl_3 < BBr_3$. There are gross electronic similarities between SnX_2 and BX_3 compounds, the most obvious of which is the six-electron valence shells surrounding the central atoms. In BX_3 molecules, all three electron pairs are bonding, while in SnX_2 one lone pair and two bonding pairs surround the tin. Both species nominally have empty valence p orbitals. To the extent that these similarities are electronically significant, we may anticipate parallel behavior of these two types of species as Lewis acids. In addition it is noteworthy that tin also possesses empty valence d orbitals which may be energetically accessible for use in acceptor bonding. Their presence gives tin the potential to act as a multifunctional Lewis acid site whereas boron usually does not. The known[1,9] adducts of tin halides with multidentate ligands provide evidence for such bonding although there is not full agreement on how the multifunctional bonding occurs.

In general, the synthesis of stoichiometric trimethylamine adducts was most readily carried out for tin(II) iodide and was most difficult for tin(II) fluoride. Both the mono- and bis(trimethylamine) adducts of SnI_2 formed rapidly and quantitatively by direct combination of the components in *p*-dioxane solution. The 1:2 adduct was reasonably stable in contact with air but the 1:1 adduct decomposed rapidly upon exposure. The 1:1 adducts of $SnBr_2$ and $SnCl_2$ formed readily under the same conditions but special conditions including an excess of amine were required to effect the synthesis of $SnF_2 \cdot N(CH_3)_3$ which was found to decompose after a few days at room temperature. The 1:2 adduct of $SnBr_2$ could be obtained by a direct combination of stoichiometric quantities of the components but the 1:2 adduct of $SnCl_2$ required an excess of amine and the 1:2 adduct of SnF_2 could be synthesized only under forcing conditions. The latter adduct lost trimethylamine readily at room temperature and so was not included in studies such as Mössbauer spectra where reasonable stability was required.

Elemental analyses supported the formulation of each adduct described above; however, the facile decomposition of adducts of the lighter tin(II) halides required that fresh samples be analyzed with protection from air and moisture during handling. The more stable adducts were also studied using differential thermal analysis (DTA) and thermogravimetry (TG) and typical curves are shown in Figure 1. Generally the TG curves of both the 1:1 and 1:2 adducts exhibited a single, fairly smooth weight loss beginning near 100 °C and tailing off above 250 °C. Separate losses of the first and second ligands were not usually visible in the 1:2 adducts. The DTA traces showed one or more endotherms in the same temperature interval. The TG and DTA curves were consistent with an initial adduct dissociation followed by a more complex decomposition–sublimation above about 130 °C.

A better assessment of the stabilities of the adducts was obtained from direct measurements of the trimethylamine pressure above the adducts in the temperature range from 40 to 120 °C. In this process measured quantities of solid adducts were placed in a chamber contained in a thermostatable oven and connected to a high vacuum line. (Adducts of SnF_2 were not included because of their instability.) The adduct in each case was held at −78 °C while the chamber was evacuated and then isolated from the vacuum line. Dissociation pressures were measured manometrically while the oven was held at 40, 60, 80, 100, and 120 °C (±0.1°) and are listed in Table II. Care was taken that the pressures became constant at each temperature and other work had shown that the dissociation of the adducts (except those of SnF_2) was reversible provided that the temperature did not exceed 130 °C.

Van't Hoff plots of the pressure and temperature data were prepared from which ΔH and ΔS values were obtained using linear regression slope and intercept values (Table III). The free energy changes associated with the decomposition at 80 °C were calculated from ΔH and ΔS (80 °C) and also directly from K_p values measured at 80 °C. The differences between the ΔG values calculated as above did not exceed 10% which corresponds well with our estimated relative error limit in the pressure measurements.

The ΔH and ΔG values for these adducts are small, indicating that the adducts are weak, compared, for example, to the trimethylamine adducts of the boron(III) halides. The enthalpy changes for dissociation decrease in the order $SnBr_2 > SnI_2 > SnCl_2$ for both the 1:1 and 1:2 adducts. The best parameter for stability comparison, however, is ΔG which at 80 °C gives the order $SnI_2 > SnBr_2 > SnCl_2$ for 1:1 and 1:2 adducts. (The most stable adducts have the least negative ΔG values.) The differences between the acceptors, although small, are significant based on our estimates of the error in ΔG.

It is noteworthy that the 1:2 adducts are in all cases less stable than the 1:1 adducts of the same acceptor. This is generally expected on electronic grounds considering charge buildup on the tin. Also, the order of ΔG values closely parallels the difficulty experienced in synthesizing the adducts, a surprising result in view of the pivotal role often played by kinetic factors in synthesis.

The heats of adduct formation between tin(II) halides and trimethylamine are much smaller than those of analogous boron(III) halides[10] but the order of adduct stabilities parallels that mentioned earlier for the BX_3 acceptors with nitrogen bases. Probably the most convincing rationale for the fact that this order is opposite that expected from consideration of the inductive effect of the halogens has been proposed by Drago.[11] It recognizes a competition between π bonding in the boron–halogen bond and σ bonding in the boron–donor atom bond for the vacant boron valence orbital. In BF_3 adducts where intramolecular π overlap is significant, it occupies the boron acceptor orbital to the detriment of the donor–acceptor bond. Conversely BCl_3 and BBr_3 are stronger acceptors because inefficient π overlap in the B–X bonds leaves the vacant boron orbital free for strong σ acceptor bonding.

Considering the relative size of the tin 5p orbitals and the greater Sn–X distances, it seems improbable that effective π overlap could occur between tin and halogen p–π orbitals. For this reason the foregoing rationale seems incapable of accounting for the order of SnX_2 adduct stabilities. Another possible reason for the greater stability of the adducts of the tin(II) iodide and bromide involves bridging halogens.[12] If the greater polarizability of the heavier halogens results in their forming stronger halogen bridges in the adducts, this factor might account for the increased stability of those adducts. In view of the relatively small differences in ΔG, it may not be possible to provide an obvious rationale without additional information.

The ^{119}Sn chemical isomer shift (relative to $BaSnO_3$) obtained for the tin(II) halide–trimethylamine adducts are given in the Experimental Section; no quadrupole splitting was observed in the spectra of any of the adducts. The SnF_2 adducts were omitted because of their instability. It is generally accepted[13] that ^{119}Sn isomer shifts (IS) reflect changes in the 5s electron density on tin. Previous studies[14] of tin(II) halide adducts with various donors have shown that the Mössbauer signals of the adducts occur at lower velocity (smaller isomer shift) than those of the parent tin(II) halide. The decrease in IS which accompanies adduct formation is unexpected because it implies a decrease in 5s electron density. It has been rationalized[14] by invoking an increased participation of the 5s orbital and electrons in s–p hybridization upon formation of the adduct. The assumption is made that covalent utilization of the 5s electrons decreases the electron density at the tin nucleus. However, the hybridization of SnX_2·donor and SnX_3^- species is interpreted as s–p by some authors[15] and as p^3 by another.[16] The small $5s^2$ to $5s^15p^1$ promotion energy (6.64 eV) is cited as a compelling reason for s–p mixing while the near-90° bond angles in SnX_3^- ions are interpreted to indicate essentially p^3 hybridization. Lacking structural parameters for the trimethylamine adducts, we find it reasonable to accept the s–p hybridization rationale for the negative isomer shift. In itself, however, it does not imply a linear relationship between adduct stability and ΔIS.

Even without a convincing rationalization for the direction of the IS change, some aspects of its magnitude are of interest.

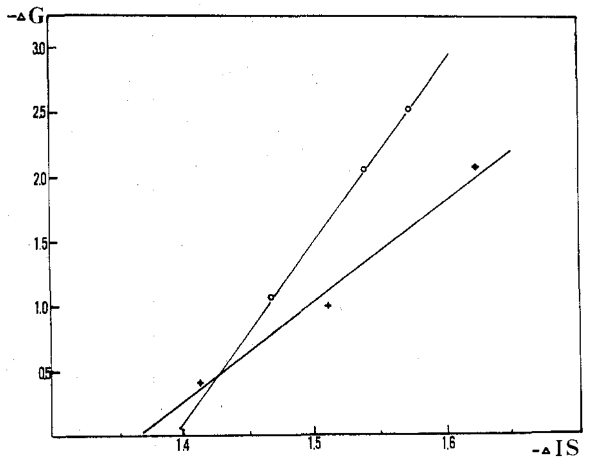

Figure 2. Free energy (kcal mol^{-1}) vs. complexation isomer shift (mm s^{-1}) for tin(II) halide–trimethylamine adduct dissociation: + = 1:1 adducts, ○ = 1:2 adducts.

Table IV. Mössbauer Isomer Shifts of Tin(II) Halide–Trimethylamine Adducts

Compd	IS, mm s^{-1} [a]	ΔIS, mm s^{-1} [e]
$SnCl_2$	4.15	
$SnBr_2$	4.06[b]	
SnI_2	3.98[b]	
$SnCl_2 \cdot N(CH_3)_3$	2.53 (0.02)[c]	−1.62
$SnBr_2 \cdot N(CH_3)_3$	2.55 (0.02)[c]	−1.51
$SnI_2 \cdot N(CH_3)_3$	2.57 (0.02)[c]	−1.41
$SnCl_2 \cdot 2N(CH_3)_3$	[2.58][c,d]	[−1.57][d]
$SnBr_2 \cdot 2N(CH_3)_3$	2.52 (0.02)[c]	−1.54
$SnI_2 \cdot 2N(CH_3)_3$	2.51 (0.02)[c]	−1.47

[a] $Ba^{119m}SnO_3$ source. [b] Data from ref 16. [c] Source and absorber at 298 K. [d] Value suspect because of adduct instability over periods in spectrum data accumulation. [e] $\Delta IS = IS(adduct) - IS(SnX_2)$.

It was first suggested by Donaldson et al.[14] that the difference between the isomer shift of the complex and its parent acceptor could indicate the strength of the tin–ligand bond. Although the earlier investigators did not report data to assess the quantitative aspect of this relationship, we have found a rather striking correlation (Figure 2) between the complexation Mössbauer shifts (ΔIS) and the free energy changes for adduct formation obtained in our studies. Although the number of data points is presently too limited to serve as the basis for wide generalization, there is strong possibility that complexation isomer shifts will provide useful information on adduct stabilities. If we adopt the convention that

$$\Delta IS = \delta SnX_2 \cdot donor - \delta SnX_2$$

then the most stable adducts (i.e., those with least negative ΔG for dissociation) also have the least negative ΔIS. The linear regression lines for the 1:1 and 1:2 adducts shown in Figure 2 fit the equations shown below with $R = 0.999$ and $R = 0.999$, respectively.

$$\Delta IS(1{:}1) = 0.136(\Delta G) - 1.352$$

$$\Delta IS(1{:}2) = 0.081(\Delta G) - 1.377$$

Using the above criterion we may compare adduct stabilities where trimethylamine is the ligand with those where pyridine is the ligand. We calculate ΔIS values of −0.77 and −0.39 mm s^{-1} for $SnCl_2 \cdot C_5H_5N$ and $SnBr_2 \cdot C_5H_5N$ from ref 14 which indicates that the order of adduct stabilities is $SnBr_2 > SnCl_2$ in agreement with our results but opposite the order interpreted in that paper. Comparing the ΔIS values for the pyridine adducts with those of the trimethylamine adducts (Table IV) of the same acceptor suggests that the latter are weaker. Also the 1:2 adducts in both the earlier report and the present study have more negative ΔIS values than the 1:1 adducts indicating the expected decrease in stability. The difference is small probably suggesting that the second ligand is bound much more weakly than the first. We are presently investigating other adducts of tin(II) halides to determine how widely the observed ΔG–ΔIS relationship holds.

The relatively low solubility of the tin(II) halide adducts hampered solution studies of the compounds. Small solubility was found in aniline and some more polar solvents but the latter caused loss of trimethylamine apparently via displacement reactions especially in the case of the 1:2 adducts. Aniline was satisfactorily employed as a solvent for ^{1}H NMR studies of the 1:1 adducts which gave singlets for methyl proton resonances with the chemical shifts noted in the Experimental Section. In the case of the boron(III) halide–trimethylamine complexes, methyl proton chemical shifts are reported[8f] to reflect adduct stabilities, so it was of interest to ascertain whether any similar relationship exists in the $SnX_2 \cdot N(CH_3)_3$ adducts. The chemical shifts of the 1:1 species give a reasonably good linear correlation ($R = 0.994$) when plotted vs. ΔG. The validity of the correlation assumes the absence of ligand exchange processes but this was not proven experimentally. Again, the limited data available mitigate against broad interpretation of the relationship at the present time but it is, nevertheless, interesting that even a limited correlation should exist between proton magnetic resonance and Mössbauer isomer shifts in adducts such as these. Evidently both these parameters are directly influenced by the same flow of charge which gives rise to the donor–acceptor bonding.

NMR parameters are not presented for the 1:2 adducts because there was evidence from time-dependent changes in the NH_2 protons of the solvent (aniline) that dynamic processes were occurring in those solutions. The nature of these reactions has not yet been elucidated.

It was hoped initially that the infrared spectra of the adducts would also provide information concerning the strengths of the donor–acceptor interaction in the adducts. However, no sensible interpretation of the IR band complexation shifts, etc., could be made, in part because positive assignment of tin-nitrogen stretching modes was not possible with the instrumentation available. Strong broad bands were observed between 500 and 600 cm^{-1} which appeared to be associated with adduct formation. We may note in this regard that Donaldson et al.[14] also reported problems in the interpretation of IR spectra of the pyridine adducts of $SnCl_2$ and $SnBr_2$.

Acknowledgment. The authors gratefully acknowledge the support of this investigation by the Robert A. Welch Foundation under Grant E-439. We are also grateful to Professor Mary Good for providing us with information regarding Mössbauer spectra of tin(II) complexes prior to publication. Special thanks are due Dr. Wesley Wendlandt for obtaining the TG and DTA spectra and Dr. Wayne Wentworth for helpful discussions. We also appreciate the help given by Dr. Denny Lee, University of Houston, Physics Department, in the use of his Mössbauer spectrometer.

Registry No. $SnF_2 \cdot N(CH_3)_3$, 63528-07-4; $SnCl_2 \cdot N(CH_3)_3$, 63528-08-5; $SnBr_2 \cdot N(CH_3)_3$, 63528-09-6; $SnI_2 \cdot N(CH_3)_3$, 63528-10-9; $SnF_2 \cdot 2N(CH_3)_3$, 63528-11-0; $SnCl_2 \cdot 2N(CH_3)_3$, 63528-12-1; $SnBr_2 \cdot 2N(CH_3)_3$, 63528-13-2; $SnI_2 \cdot 2N(CH_3)_3$, 63528-14-3; SnF_2, 7783-47-3; $SnCl_2$, 7772-99-8; $SnBr_2$, 10031-24-0; SnI_2, 10294-70-9.

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Magnetic Properties of Oxygen-Bridged Binuclear Chromium(III) Complexes with 2,2′-Bipyridine and 1,10-Phenanthroline

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Received February 14, 1977 AIC70116T

Magnetic susceptibilities of dimers of the type $[(N\text{-}N)_2Cr(OH)_n(O)_{2-n}Cr(N\text{-}N)_2]^{n+2}$ (n = 2, 1, 0; N-N = 2,2′-bipyridine or 1,10-phenanthroline) have been measured within the temperature range 5–300 K. The results are interpreted in terms of an antiferromagnetic coupling giving singlet–triplet separations ranging from ca. 40 cm^{-1} (n = 2) to ca. 110 cm^{-1} (n = 0). For n = 2 the data were fitted by least squares to the Heisenberg isotropic exchange model. Inclusion of a biquadratic exchange term did not improve the fitting significantly. Slightly different coupling constants were found for different salts of the phenanthrolinediol (n = 0). Via the angular overlap model the results are compared with the antiferromagnetism in the μ-oxo-bis{pentaamminechromium(III)} ion.

Introduction

A number of papers from this laboratory[2–7] have dealt with oxygen-bridged polynuclear complexes of chromium(III) and cobalt(III), including studies of their molecular and crystal structures[2–4,6] and their spectral and magnetic properties.[6,7] Among the complexes were salts of $[Cr(N\text{-}N)_2OH]_n{}^{2n+}$, having N-N = 2,2′-bipyridine and 1,10-phenanthroline,[5] which were shown to be binuclear and thus to belong to the class of structures called diols.[5] Since these two chromium diols are rather robust over a wide pH range, it was possible to isolate and characterize[5] the perchlorates of the novel complex cations of the types μ-hydroxo-μ-oxo-bis[bis(N-N)chromium(III)] and